SCIENCE FOR GLASS PRODUCTION

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MODIFICATION OF THE SURFACE OF SHEET GLASS (A REVIEW)

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The paper contains an analysis of the literature data on modification of the surface of sheet glass in order to impart heat-shielding, conducting, hydrophobic, x-ray-shielding, decorative, and other properties to glass. Various industrial and scientific entities engaged in production and development of modifying coatings are described. A classification of film coatings is offered, and the main production methods are considered. The effect of various factors on film coatings is analyzed.

Improvement of physicochemical, spectral, electric, and other properties of sheet glass using various coatings is a promising and comprehensive goal. At the same time, industrial recycling of sheet glass is essential both in our country and abroad. The main achievements of foreign researchers in this field are described in [1]. The present review is based on an analysis of domestic research. Such studies have been carried out in Russia for some time with considerable success [2, 3]. Film-forming solutions and technology and instruments for their deposition have been developed, and the coating formation mechanism has been studied and described. However, judging from the product range offered on the market, implementation under industrial conditions virtually has not happened.

Production of sheet glass with a modified surface is related to wide possibilities for varying glass properties and to cost effectiveness not only in the case of continuous production but also in the case of industrial recycling of limited quantities. The "Stroiexpo-99" Exhibition of Construction Materials in Belgorod indicated that domestic manufacturers are starting to develop the market. The Iri Company (Kazan) exhibited various glasses with an optically selective coating that possess energy-saving and solar radiation-protective properties. These glasses were obtained by industrial recycling of sheet glass.

An interesting development of a highly efficient composition with electrically controlled light dissipation based on glass, liquid crystals, and polymer coatings ("intelligent windows") was offered by Naukoemkie Tekhnologii JSC (Orel) together with the State Institute of Glass (GIS), Moscow. The field of application for such coatings consists in protection from electromagnetic radiation and production of energy-saving and non-freezing composites.

The Saratov Institute of Glass has developed coatings with various spectral characteristics and deposition methods. The coating are deposited by continuous spraying in the course of sheet-glass production and recycling [4]. The development of infrared technology and its wide application in various fields have contributed to research and development of interference coatings. The Tekhnologiya Research and Production Association (Obninsk) is developing antiglare and clarifying coatings for the infrared spectral range [5].

Recently the demand for sheet glass with various properties has increased significantly. This is due to the new requirements imposed on building design, in which the surface area of glazing has grown to 80%. A similar tendency exists in machine-building and the manufacture of cars. The tendency for reduced weight and a streamlined shape for modern cars and the creation of a better view range and better comfort for the driver and passengers call for an increased area of car glazing using polyfunctional glass [6].

A wide range of construction and engineering glass has been developed using thin film coatings.

The developed methods for glass-surface modification include thermochemical treatment with gas reactants, deposition of protective film coatings using the sol-gel method, and deposition of heat-shielding coatings by cathode metal spraying in vacuum. Several devices and methods for applying modifying coatings to the glass surface have been developed and patented (Polish patent No. 157225, USSR patents

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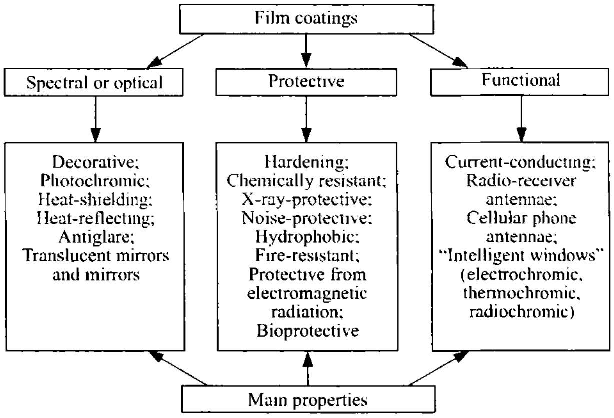
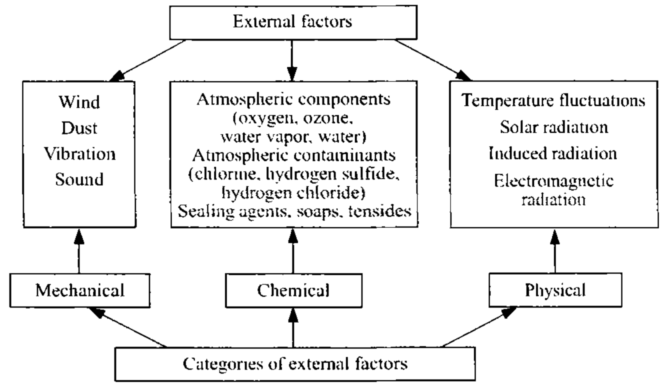


Scheme 1



Scheme 2

Nos. 1571016 and 923985; U.S. patents Nos. 5514485 and 2298519).

A classification of glasses based on their areas of application and main properties in shown in Scheme 1.

Film coatings are distinguished by a number of physical properties determined by many factors: the chemical nature of the component, the methods and conditions of synthesis, the nature of the substrate on which the film condenses, the thickness, etc. These main properties, which include optical, electrical and strength parameters, are inherent in the overwhelming majority of film coatings.

The optical properties of glass with film coatings and those of glasses without coatings are characterized by the indices of light transmission, reflection, and radiant-energy absorption. The transmission of films depends on their degree of absorption and reflection. The absorption of clear films (heat- and current-conducting) is insignificant: only 1 – 3% in the visible spectral range, and in the infrared range, it increases proportionately to the conductivity. Heat-reflecting glasses with transparent coatings, which are heated to a lesser degree, are the most effective as protection from solar radiation. The electrical properties of coatings can be evaluated based on their electrical conductivity [7 – 9].

An improvement in the physicomechanical parameters of the surface and an increase in the strength can be achieved by depositing various polymer liquids, hardening in a ferromagnetic coolant liquid, thermochemical modification, and ion exchange in the course of glass production [10 – 16].

Hardening of the surface of sheet glass by ion exchange is based on diffusion of ions, which results in a change in the chemical composition and properties of the surface due to introduction of new ions from solutions and melts. The ion-exchange process can be intensified by various methods: selection of the chemical composition of the glass, the time and temperature conditions, and the salt-bath composition, treatment in the electric field of a direct or alternating current and in high-temperature energy fields (plasma-electron treatment) [17, 18].

The mechanism of the hardening effect of polymer coatings on a glass surface is apparently determined by the combined effect of the following main factors [10]: healing of surface microdefects to a certain extent by closing microcracks and blocking their further development, creation of reliable physicochemical protection from the action of weakening reactants. The polymer liquids are lacquers, epoxy resins, etc. (USSR patents Nos. 2089520, 2089521, and 2089522, U.S. patent No. 5487920) and organosilicon liquids [19].

Interest in organosilicon compounds used to improve the service properties of glass has been growing steadily of late, since coatings based on organosilicon compounds have a wide spectrum of functional properties, from hardening and decorative properties to controlled light dissipation, bioprotection, and protection from electromagnetic radiation [20 – 23].

Finally, the appearance of so-called "intelligent windows" is directly related to the ability of functional pigments to reversibly change their color and properties, depending on certain external factors: protochromic and chameleon glasses depend on light, thermochromic glasses depend on heat, electrochromic glasses and antiglare mirrors depend on electric fields, and radiochromic and dosimeter glasses depend on radioactive radiation (U.S. patents Nos. 5480722 and 5585959). The development of such multilayer coatings based on oxides of various metals and polymer components is a promising field for Russian researchers.

The engineering properties of the coatings are determined by their area of application and service conditions. Of great importance is the mechanical strength of the films, their adhesion to the glass, and their resistance to atmospheric exposure.

Scheme 2 lists the main factors that influence the state of film coatings. They are not equal in the extent of their action. Moreover, the effects of various factors on a glass surface are often superimposed.

Since it is difficult to determine directly the strength of a film coating, the capacity of a film for polishing under certain (standard) conditions has been taken as the strength cri-

terion of the film. The effect of atmospheric factors on the service life of specific types of film coatings is investigated using a weatherometer in which glass samples are subjected to heating, moistening, and ultraviolet radiation. The samples removed from the weatherometer are frozen in a freezer chamber at a temperature of – 15°C with subsequent defrosting in water at a temperature of + 20°C [24, 25]. The chemical resistance of film coatings is determined by the change in the film thickness after a hold of 24 h in H_2O or 30 min in a 0.1 N HCl solution [26].

Studies performed at the State Institute of Glass (GIS) showed that films produced at high temperatures have a more perfect crystalline structure, are more transparent, have better adhesion to the glass surface, and are more resistant to various actions, and current-conducting films have better electrical conductivity [27].

By their chemical composition, film coatings are divided into metal oxide, polymer, and organosilicon types.

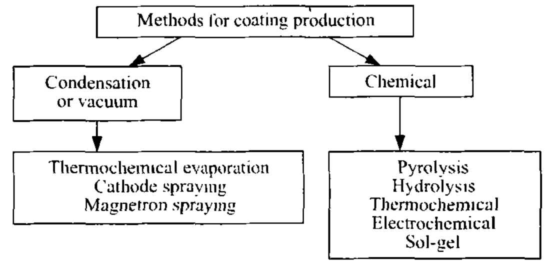
The main properties, including optical, electrical, and strength parameters, are also inherent in the vast majority of metal oxide film coatings.

Modifying oxides and metals	**Areas of application**
SnO_2, Cr_2O_3, Fe_2O_3, Fe_2O_3(Sn), CuO, Co_3O_4	Absorption of solar ultraviolet radiation
SnO_2 (Sb), (Fe_2O_3·FeO), SnO_2 (Bi), Cr_2O_3	Selective transmission in the visible spectral range (tinted, toned)
SnO_2 (Sb), Fe_2O_3, FeO, Co_3O_4	Retaining some solar thermal radiation (heat-shielding)
SnO_2 (Sb), SnO_2 (N, F), Au, Ag, Cu, Ni, SiO_2	Reflecting longwave IR radiation (heat-reflecting)
TiO_2, Fe_2O_3, CuO, Co_3O_4, Al_2O_3, GeO_2, ThO_2, WO_3	High reflection in the visible range (mirrors and semi-transparent mirrors)
SnO_2 (Sb), SnO_2(N, F), In_2O_3, In_2O_3 (Sn, F), ZnO, ZnO (In), MoO_3, V_2O_5, WO_3	Current-conducting, radioprotective, protecting from electromagnetic radiation

As can be seen, many films based on various oxides are polyfunctional. For instance, tin oxide coatings and compositions based on them not only have various spectral characteristics but also are hardening and current-conducting.

Two types of heat-reflecting glasses with transparent coatings are known: coatings containing iron, cobalt, chromium, nickel, and silicon oxides, which are deposited on the glass surface in production, and metal coatings based on gold, copper, silver, nickel, and various metal alloys, deposited employing vacuum technology (USSR Inventor's Certif. No. 1799856, RF Inventor's Certif. No. 2000280).

Light-reflecting coatings are most often produced by multilayer deposition, and the total thickness of the coating comprises several micrometers (USSR Inventor's Certif. Nos. 6140050 and 726044). Such a coating includes metals and an additional layer with a refractive index of 1.85 – 2.00, which can be made of zirconium or tin oxide.



Scheme 3

Besides pure reactants, metal-bearing wastes can be used to modify glass surfaces. Methods for utilization of wastes (organic, metallurgical, and by-product coke industry) and compositions for film-forming solutions based on them are proposed in [28]. Industrial testing and implementation of this technology in continuous and batch glass-melters not only allows savings in power and material resources but also improves the environmental situation in industrial regions (USSR Inventor's Certif. No. 1449552).

Sol-gel oxide coatings are amorphous materials whose nature is similar to glass. However, their extremely small thickness (down to hundreds of angstroms), the presence of pores, the low temperature of synthesis, and diffusion processes at the coating-glass interface introduce significant differences in structure formation. The literature data on the sol-gel process implemented through alkoxide technology are highly diverse: beginning with the study of the process of formation of SiO_2 powders and films from film-forming solutions and ending with doping of vitreous films of silicon oxide with dopants of B, P, Sb, As, Zn, Co, and various metal oxides [22, 29 – 32].

Use of organosilicon compounds to improve glass properties, in particular, hydrophobic properties, is based on formation of a polyorganosiloxane film on the glass surface. Organosilicon compounds are usually classified in two large groups: low-molecular-weight and high-molecular-weight. The classification of these compounds is based on silanes (silicon hydrides) with the common group Si_nH_{2n+2}. Such a film is a combination of organic radicals and siloxane groups [33].

In this context, it is possible to distinguish organosilicon polymers with two reaction groups. The essence of the method for producing a tinted coating consists of two-stage grafting of compounds: first to the glass surface and then grafting of the main organic colorant (USSR Inventor's Certif. No. 1350131). Of greatest interest are bifunctional organosilicon compounds with easily hydrolyzing groups.

All existing methods for film deposition can be split into two groups. The first includes vacuum or condensation methods, and the second is based on various chemical reactions occurring on the glass surface (Scheme 3). The vacuum methods require costly and energy-consuming equipment and do not always ensure chemically resistant and mechanically strong films.

Metal oxide and metallic film coatings 0.3 – 1.0 μm thick are usually produced by evaporation (precipitation) of metals in vacuum or fine spraying of hydrolyzing of metal salts solutions at a temperature close to the glass softening point (USSR patents Nos. 1359261 and 2298519). The hydrolysis reaction starts at the moment when the initial material in the form of a vapor (pyrolysis method) or a solution (pulverization and immersion method) reaches the hot glass surface.

A method currently used abroad is electrochemical deposition of a tinted film directly in the melting tank in the course of float production of sheet glass [33, 34].

An increase in the chemical resistance and mechanical strength of multicomponent industrial silicate glasses can be achieved by thermochemical modification using hydrocarbon vapors that comprise the basis of heavy fractions of oil refining. It is established that naphthenic and aromatic hydrocarbons are less effective than saturated hydrocarbons (*n*-hexane, *n*-heptane, 1-hexene). Aromatic compounds in modification create a protective coating on the surface whose reacting mechanism is based on the decomposition of lateral alkyl radicals in heat treatment and their reaction with oxygen, which facilitates the fixation of the coating on the surface. The benzoic ring in this case imparts additional hydrophobic properties to the glass [34].

Another promising field in contemporary materials science is related to sol-gel synthesis of coatings and materials for different functional purposes. An advantage of this technology consists in the possibility of creating conditions for component reactions at the level of molecular dispersion at low temperatures. This makes it possible to significantly reduce the activation energy of the process and obtain materials with a high degree of homogeneity and a prescribed chemical composition over a wide concentration range [22, 25].

Additional advantages of the sol-gel method include simplicity of deposition of film-forming solutions using such methods as immersion, centrifuging, aerosol spraying, and relatively low capital investments in equipment [35].

Transformation of organometallic polymer gel into the corresponding metal oxide is effected using either the pyrolysis method or heat treatment at 450 – 600°C. In the second case, to ensure a uniform coating layer, the solution is applied mainly by immersion and centrifuging.

The effect of diffusion, the age of the solution, and structural phase transformations on the properties, quality, and technological parameters of films of the $Bi_2O_3 - Fe_2O_3 - TiO_2$ and $CuO - TiO_2$ systems was studied in [36]. The production of large-sized glass sheets with a heat-reflecting coating based on an $SiO_2 - Fe_2O_3$ film-forming solution has been implemented at the Avtosteklo Production Company (town of Konstantinovka). The glass was immersed in a tank filled with the solution. After a 3-min hold, the solution was poured off, and the glass sheet was removed and placed in a polycondensation chamber for 30 min at a temperature of 450 – 500°C. The resulting film thickness was controlled by varying the solution outflow rate.

Thus, an analysis of the domestic literature on modification of the surface of sheet glass revealed that scientists in Russia and the CIS are carrying out intense research and development of coatings for various purposes . Judging from the technologies implemented and the products offered on the market, foreign producers are ahead of our research and production practices. A promising goal for Russian science consists in fundamental studies in the field of polyfunctional thin films and the development of multilayer coatings based on various metals and polymer components. Various chemical methods for producing thin-layer coatings play an increasingly important role in this process.

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